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INTERATOMIC FORCES AT VERY SHORT RANGE *

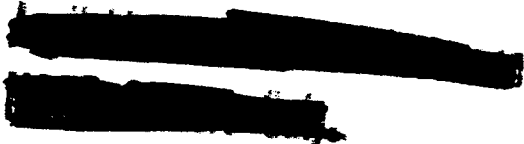
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ABSTRACT

The subject of this paper is the theoretical analysis of the electronic energy $W(R)$ of two interacting atoms in powers of the interatomic distance R . A new approach is presented based on the Hellmann-Feynman theorem for the electronic force dW/dR , which is written as a sum of integrals over Legendre components of the electron density expressed in elliptic coordinates. Analysis of the first two components yields the formula previously obtained by Bingel for the coefficient W_2 of R^2 , but a new formula for W_3 which replaces that found by Bingel using perturbation theory.



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INTRODUCTION

The total potential energy of two atoms A and B at a fixed distance R apart may be written

$$E(R) = W(R) + z_a z_b / R \quad (1)$$

where W is the electronic energy and z_a, z_b are the charges on the nuclei. At extremely short range the interaction is dominated by nuclear repulsion. As R increases, the change in electronic energy with distance begins to play a role, and to describe this effect it is natural to express W as a power series in R :

$$W(R) = E_0 + R^2 W_2 + R^3 W_3 + R^4 W_4 + \dots \quad (2)$$

In this equation $W(0) = E_0$ is the energy of the united atom with nuclear charge $Z = z_a + z_b$, and the coefficients W_2, W_3 , etc., are properties of the united atom which may be investigated theoretically. Since W approaches a finite limit, $W(\infty)$, the sum of the energies of the separated atoms, such a series inevitably has only a very short range of validity. In fact, it is not possible to obtain the coefficients W_2 , etc., directly from atomic beam scattering measurements, as these very small distances are inaccessible with present techniques. At the shortest range accessible at present

the repulsion can be fairly well represented by a simple exponential term $C \exp(-\alpha R)$. In order to bridge the gap between the short range exponential behavior and the very short range interaction described by equations (1) and (2), Buckingham¹ therefore proposed the form

$$E(R) = \frac{Z_a Z_b}{R} p(R) \exp(-\alpha R), \quad (3)$$

where $p(R) = 1 + p_1 R + p_2 R^2 + \dots$ is a polynomial in R . If the exponent α is given, and some of the coefficients E_0, W_2, W_3 , etc., are known from united atom properties, then equation (3) can be used to replace the constant C , and semi-empirically to extend the range of the simple exponential form.

The subject of this paper is the quantum mechanical theory of equation (2). Buckingham¹ pointed out that the first-order coefficient W_1 always vanishes exactly, even for many-electron heteronuclear molecules. Bingel² obtained general expressions for the coefficients W_2 and W_3 , relating them to simple properties of the united atom. However, in attempting to develop the theory further, Steiner³ and I discovered an inconsistency in Bingel's treatment of W_3 , and found that the corresponding formula for W_4 diverged. These conclusions were confirmed by Levine.⁴ Furthermore, Steiner and I⁵ and Levine⁶ obtained the exact W_3 and W_4 (finite) for the one-electron case, and Duparc and Buckingham^{7,8} obtained

approximate values of W_2 and W_3 for two, three and four-electron systems. In all cases Bingel's formula for W_3 was clearly wrong.

The further development of the theory of the united atom expansion (2) therefore hinges on the coefficient W_3 . It can be shown that the perturbation treatment used by Bingel is incapable of yielding the form of W_3 in the general case of many-electron atoms. The existence of an R^3 term in W , and the stumbling block for the theory, is due to the non-analytic behaviour of the electron density at the nuclei of atoms and molecules. Although the existence of cusps at the nuclei is well known, the consequence of the coalescence of two cusps as $R \rightarrow 0$ have been overlooked.

A new approach is therefore needed which can adequately handle the mathematical singularities involved. The object of this paper is to describe an approach which enables the general form of W_3 to be obtained.

HELLMANN-FEYNMAN THEOREM FOR ELECTRONIC FORCE

According to the Hellmann-Feynman theorem¹⁰, the force attracting nuclei A and B together due to the electrons is

$$\begin{aligned} \frac{dW}{dR} &= \left\langle \Psi, \frac{\partial H}{\partial R} \Psi \right\rangle, \\ &= - \int \rho(\mathbf{r}; R) \frac{\partial}{\partial R} \left(\frac{Z_a}{r_a} + \frac{Z_b}{r_b} \right) d\tau, \quad (4) \end{aligned}$$

where $\rho(r; R)$ is the exact electron density in the molecular system AB, and r_a, r_b are the distances of the integration point r from A, B. The precise form of the force operator in the integrand of (4) depends upon the electronic coordinates held fixed during the differentiation, and in particular on the coordinate origin; the value of dW/dR is, of course, independent of the choice. It is very convenient, for a reason which will become apparent shortly, to take the origin to be the center of nuclear charge C; that is, on the line AB at a distance $R_a = Z_b R / Z$ from atom A and $R_b = Z_a R / Z$ from atom B, as illustrated in Figure 1. The electronic force (4) then becomes

$$\frac{dW}{dR} = \frac{Z_a Z_b}{Z} \int \left(\frac{\cos \theta_a}{r_a^2} + \frac{\cos \theta_b}{r_b^2} \right) \rho(r; R) d\tau, \quad (5)$$

where the angles θ_a, θ_b are defined in Figure 1.

It is shown in the next section that the behavior of the electron density ρ in the vicinity of the nuclei can be very simply described by using confocal elliptic coordinates ξ, η defined by

$$\xi = (r_a + r_b) / R, \quad \eta = (r_a - r_b) / R. \quad (6)$$

It is therefore convenient[†] to regard ρ as a function of

[†] The electron density for a linear molecule in a spectroscopic state is independent of the azimuthal angle ϕ .

and $R : \rho = \rho(\xi, \eta; R)$. In terms of elliptic coordinates the electronic force (5) becomes

$$\frac{dW}{dR} = \frac{Z_a Z_b}{Z} 2\pi R \int_{-1}^{\infty} d\xi \int_{-1}^{+1} d\eta f(\xi, \eta) \rho(\xi, \eta; R), \quad (7)$$

where

$$f(\xi, \eta) = \frac{1}{2} \left[\frac{(1+\xi\eta)(\xi-\eta)}{(\xi+\eta)^2} + \frac{(1-\xi\eta)(\xi+\eta)}{(\xi-\eta)^2} \right]. \quad (8)$$

The advantage in choosing the center of nuclear charge as origin is now apparent: $f(\xi, \eta)$ is an even function of η , so that only the symmetric η -component of ρ is required in the integrand.

The "force" operator f may be expanded in a series of even Legendre polynomials in the variable η :

$$f(\xi, \eta) = \sum_{\substack{l=0 \\ (\text{even})}}^{\infty} f_l(\xi) P_l(\eta), \quad (9)$$

where

$$f_l(\xi) = (l + \frac{1}{2}) \int_{-1}^{+1} f(\xi, \eta) P_l(\eta) d\eta. \quad (10)$$

To obtain a general expression for the force component f_l , write f in the form

$$f(\xi, \eta) = \frac{1}{2} \left[-2\xi + (3\xi^2 - 1) \left\{ \frac{1}{\xi + \eta} + \frac{1}{\xi - \eta} \right\} - 2\xi(3\xi^2 - 1) \left\{ \frac{1}{(\xi + \eta)^2} + \frac{1}{(\xi - \eta)^2} \right\} \right]. \quad (11)$$

The integrals required in (10) involve the Legendre functions of the second kind, Q_l , since¹¹

$$Q_l(\xi) = \frac{1}{2} \int_{-1}^{+1} \frac{P_l(\eta)}{\xi - \eta} d\eta = (-1)^{l+1} Q_l(-\xi). \quad (12)$$

The result[†] is $f_l = 0$ for l odd, and for l even

$$f_l(\xi) = (2l+1) \left[-\xi \delta_{l0} + \{ (2l+3)\xi^2 - 1 \} Q_l(\xi) - 2\xi l Q_{l-1}(\xi) \right]. \quad (13)$$

In particular

$$\begin{aligned} f_0(\xi) &= (3\xi^2 - 1) Q_0(\xi) - 3\xi, \\ &= 2 Q_2(\xi). \end{aligned} \quad (14)$$

On substituting (9) into equation (7) it becomes

$$\frac{dw}{dR} = \frac{z_a z_b}{z} 4\pi R \sum_{k=0}^{\infty} (4k+1)^{-1} \int_1^{\infty} f_{2k}(\xi) f_{2k}(\xi; R) d\xi, \quad (15)$$

[†] Equation (13) for f_l could be further reduced by eliminating the factors ξ by means of the common recurrence relation for Legendre functions of both kinds. However, the main interest in this paper is in the first few components, and the occurrence of Q functions of negative degree is inconvenient; for instance $l Q_{l-1} = 1$ for $l = 0$.

where p_{2k} are the Legendre η -components of ρ defined by

$$p_2(\xi; R) = (2 + \frac{1}{2}) \int_{-1}^{+1} \rho(\xi, \eta; R) P_2(\eta) d\eta. \quad (16)$$

In order to obtain general expressions for the coefficients W_2, W_3 , etc., in the united atom expansion (2), it is next necessary to investigate the behaviour of the molecular density components, $p_{2k}(\xi; R)$, for small values of R .

CUSP BEHAVIOUR OF ELECTRON DENSITY

The crux of the problem of obtaining W_3 is to describe correctly the singularities in ρ as $R \rightarrow 0$. The behaviour of the electron density as R becomes small and finally zero is illustrated in Figures 2. These figures may be regarded as perspective sketches of three-dimensional surfaces in which $\rho(\xi, \eta; R)$ is plotted vertically over a $\xi\eta$ -plane through the molecular axis. The change on going from (a) \rightarrow (c) can be described best in the language of mountaineering: for ordinary values of R (Figure a) the mountain landscape consists of two pinnacles A and B, separated by a col; when R has decreased to a very small value (Figure b) the peaks are now higher and joined by a sharp \hat{a} re \hat{t} e; finally when R is zero (Figure c) the separate peaks A and B have coalesced to form a conical grand pic at C.

The critical feature for the evaluation of W_3 is the line

singularity between A and B for very small (actually infinitesimal) R . To describe this feature by means of spherical polar coordinates r, θ with origin C, as Bingel's approach attempts to do, requires an infinite series of Legendre polynomial in $\cos \theta$. This is also true for spherical polar coordinates r_a, θ_a origin A, and r_b, θ_b origin B. On the other hand, the behaviour is as easily described in terms of the elliptic coordinates ξ and η , as an atomic cusp is described by the radial coordinate r .

It is shown in the appendix that the zero η -component of the electron density in a diatomic molecule satisfies the following cusp or boundary condition:

$$\left(\frac{\partial \rho_0}{\partial \xi} \right)_{\xi=1} = -RZ \rho_0(1;R) + O(R^2) \quad (17)$$

Equation (17) is the obvious generalization of the cusp condition for the electron density $\rho_{VA}(r)$ of the united atom^{12,13}

$$\left(\frac{\partial \rho_{VA}}{\partial r} \right)_{r=0} = -2Z \rho_{VA}(0), \quad (18)$$

to which it reduces in the limit $R \rightarrow 0$; this follows from the

 Levine's⁶ successful perturbation treatment of H_2^+ required just such infinite series, which he heroically managed to re-sum.

limiting form $\frac{1}{2}R\xi \rightarrow r$. Furthermore,[†] if $\rho_0^{UA}(r)$ is the S-component of $\rho_{UA}(r)$, then through terms in R

$$\rho_0(\xi; R) \approx \rho_0^{UA}(R\xi/2), \quad (19)$$

and in general

$$\rho_{2k}(\xi; R) \approx \rho_{2k}(R\xi/2). \quad (20)$$

ELLIPTIC FORCE OPERATOR COMPONENTS

Before dW/dR can be investigated as a function of R , it is necessary to discover the behaviour of the force components, $f_e(\xi)$. They do not appear to have been discussed previously, although the use of the force operator in elliptic coordinator is quite natural, and is well known.¹⁴

The following results are readily obtained from the equations (13) and (14), by using the elementary properties¹¹ of the $Q_e(\xi)$. The zero and second components cannot always be conveniently fitted in to the general formulae, and are therefore quoted separately.

[†] The important result (19) does not follow immediately from equation (17), but requires in addition the condition

$$(\partial \rho_0(1; R) / \partial R)_{R=0} = (\partial \rho_{UA} / \partial r)_{r=0},$$

which holds for the one-electron case, and is assumed to hold in general. A similar assumption is implied in equation (20).

Small ξ : $f_l(\xi) \approx -\log(\xi-1)$, (all l). (21)

Large ξ : $f_0(\xi) \sim 4/15\xi^3 + O(\xi^{-5})$. (22)

$$f_2(\xi) \sim -2/\xi - 2/3\xi^3 + O(\xi^{-5}). \quad (23)$$

$$f_l(\xi) \sim -\frac{2^{l+1}\sqrt{\pi}}{(l-\frac{3}{2})!} (\xi)^{l-2}, \quad (l \neq 0). \quad (24)$$

Integral: $\int_1^\infty f_0 d\xi = \frac{1}{3}$. (25)

$$\int_1^\infty f_2 d\xi \text{ diverges logarithmically.} \quad (26)$$

$$\int_1^\infty f_l d\xi = -\frac{4(2l+1)(l+2)}{(l+1)(l-2)(l+3)}, \quad (l \neq 0, 2). \quad (27)$$

The first few components are plotted against ξ in Figure 3.

The points to be noticed are: (a) all the f_l diverge logarithmically to $+\infty$ as $\xi \rightarrow 1$; (b) all the f_l , except f_2 , behave asymptotically like ξ^{-3} or a higher power; (c) all the f_l , except f_2 , have finite integrals over $(1, \infty)$.

EXPANSION OF ELECTRONIC FORCE

It is now possible to return to equation (15) for the electronic force, dW/dR , and investigate its behaviour for small R . In the present paper the analysis will be confined to the first two powers of R in dW/dR . Then it follows from the results of the last two sections that the terms in (15) with $k \geq 2$ can be neglected. To show this, consider the k th term when R is small:

$$\begin{aligned} \int_1^\infty f_{2k}(\xi) p_{2k}(\xi; R) d\xi &\approx \int_1^\infty f_{2k}(\xi) p_{2k}^{UA}(R\xi/2) d\xi, \\ &= \frac{2}{R} \int_{R/2}^\infty f_{2k}(2r/R) p_{2k}^{UA}(r) dr. \quad (28) \end{aligned}$$

According to Equation (24) $f_{2k}(\xi) \sim -A_{2k} \xi^{1-2k}$ where A_{2k} is a constant. Therefore

$$(28) \rightarrow - \left(\frac{R}{2}\right)^{2k-2} A_{2k} \int_0^\infty p_{2k}^{UA}(r) r^{1-2k} dr. \quad (29)$$

The integral in (29) is finite because $p_{2k}^{UA}(r)$ behaves like r^{2k} for small r and decays exponentially for large r . Thus the term for $k = 2$ is of order R^2 , and its contribution to dW/dR is of order R^3 , which we are neglecting.

Attention can therefore be confined to the first two terms in equation (15),

$$\frac{dW}{dR} = \frac{Z_a Z_b}{Z} 4\pi R \left[\int_1^\infty f_0(\xi) \rho_0(\xi; R) d\xi + \frac{1}{5} \int_1^\infty f_2(\xi) \rho_2(\xi; R) d\xi + \dots \right] \quad (30)$$

In the first integral, $\rho_0(\xi; R)$ can be replaced by $\rho_0^{UA}(R\xi/2)$ when R is small according to equation (19). This function will change only very slowly with ξ , starting with a finite value at $\xi=1$. By contrast, $f_0(\xi)$ is infinite (but integrable) at $\xi=1$ and goes rapidly to zero like ξ^{-3} . It is therefore appropriate to expand the density as follows,[†]

$$\rho_0(\xi; R) \approx \rho_0^{UA}(R\xi/2) = \rho_{UA}(0) + \frac{1}{2} R \xi \left(\frac{\partial \rho_0^{UA}}{\partial r} \right)_{r=0} + \dots \quad (31)$$

When equation (31) is substituted into the first integral of (30), and the united atom cusp condition (18) is employed, the result is

$$\begin{aligned} \int_1^\infty f_0(\xi) \rho_0(\xi; R) d\xi &= \rho_{UA}(0) \int_1^\infty f_0 d\xi - R Z \rho_{UA}(0) \int_1^\infty \xi f_0 d\xi + \dots, \\ &= \frac{1}{3} \rho_{UA}(0) - \frac{1}{2} R Z \rho_{UA}(0) + \dots \quad (32) \end{aligned}$$

The second integral in (30) requires different treatment, because the integral of f_2 diverges. It can be handled by the technique used above for the terms $k \geq 2$:

[†] This procedure yields the first two powers of R in the expansion of the first term of (30), but the series is asymptotic only, and a different technique is required to carry the analysis further.

$$\int_1^\infty f_2(\xi) \rho_2(\xi; R) d\xi \approx \frac{2}{R} \int_{R/2}^\infty f_2(2r/R) \rho_2^{VA}(r) dr. \quad (33)$$

Now by equation (23)

$$\frac{2}{R} f_2(2r/R) \sim -2/r - R^2/6r^3 + \dots \quad (34)$$

Hence

$$\begin{aligned} \int_1^\infty f_2(\xi) \rho_2(\xi; R) d\xi &\approx -2 \int_{R/2}^\infty \rho_2^{VA}(r) r^{-1} dr + O(R^2), \\ &= -2 \int_0^\infty \rho_2^{VA}(r) r^{-1} dr + 2 \int_0^{R/2} \rho_2^{VA}(r) r^{-1} dr + \dots \\ &= -2 \int_0^\infty \rho_2^{VA}(r) r^{-1} dr + O(R^2), \end{aligned} \quad (35)$$

since $\rho_2^{VA}(r)$ is of order r^2 for small r .

Equations (32) and (35) may now be substituted into (30) to obtain

$$\begin{aligned} \frac{dW}{dR} &= \frac{Z_a Z_b}{2} \left[\frac{4\pi}{3} \rho_{VA}(0) - \frac{8\pi}{5} \int_0^\infty \rho_2^{VA}(r) r^{-1} dr \right] R - Z_a Z_b 2\pi \rho_{VA}(0) R^2 \\ &\quad + O(R^3). \end{aligned} \quad (36)$$

By differentiating equation (2),

$$\frac{dW}{dR} = 2RW_2 + 3R^2W_3 + \dots,$$

and therefore by comparison

$$W_2 = \frac{z_a z_b}{2} \left[\frac{2\pi}{3} \rho_{VA}(0) - \frac{1}{2} \int \frac{\rho_2(\cos\theta)}{r^3} \rho_{VA}(r) dr \right], \quad (37)$$

$$W_3 = -z_a z_b \frac{2\pi}{3} \rho_{VA}(0), \quad (38)$$

where the field gradient term in W_2 has been re-written as a three-dimensional integral.

The expression for W_2 is identical with that obtained originally by Bingel². However, for W_3 Bingel obtained^{2,15}

$$W_3(\text{Bingel}) = -z_a z_b \left(\frac{z_a^2 + z_b^2}{z^2} \right) \frac{2\pi}{3} \rho_{VA}(0). \quad (39)$$

The error in Bingel's perturbation treatment, which gave the entirely reasonable impression that he had obtained the complete formula for W_3 , was deep and unsuspected. It will not be discussed fully here, but it suffices to say that the perturbation expansion itself appears to be valid. The unusual feature is the behaviour of the perturbation energies as functions of R . From

the point of view of the present paper, Bingel's result can be easily derived and the error is then clear to see. The recipes for obtaining Bingel's result (39), and the correct result (38), from equation (5) for the electronic force are as follows. Let

$\rho_{UA}(r) = \rho_{UA}(r, \cos \theta)$ be the united atom electron density. Then

$$\rho^{mol}(r; R) \rightarrow \rho_{UA}(r, \cos \theta) \quad \text{leads to } W_2 \text{ and } W_3 \text{ (Bingel),} \quad (40)$$

$$\rho^{mol}(r; R) \rightarrow \rho_{UA}(R^{3/2}, \eta) \quad \text{leads to } W_2 \text{ and } W_3 \text{ (correct).} \quad (41)$$

The difference is that (41) describes correctly the non-analytic behaviour of ρ as $R \rightarrow 0$, whereas (40) only describes it for $R = 0$.

It should be added that equation (38) agrees with the exact W_3 obtained for the ground state of the one-electron system^{5,6} and also for the first few excited states.¹⁶

CONCLUSION

It is hoped that in solving the problem of the coefficient W_3 the bottleneck to the further analysis of the electronic energy expansion has been removed. The present paper shows clearly that the perturbation treatment based on the united atom, which appears so natural, is not likely to be a fruitful means of obtaining terms

in the expansion (2) beyond that in R^2 .

Whether an expansion of $W(R)$ in powers of R can be extended into the range of values at present accessible experimentally is doubtful. In any case, it has recently been shown that $W(R)$ is not in fact analytic at $R = 0$ in the one-electron case, since a term $R^5 \log R$ occurs.^{17,6} Such a term will certainly appear also in the many-electron case. However, the analysis of $W(R)$ in the vicinity of the united atom is needed to provide a basis for the theoretical discussion of the short range behaviour. One is reminded of the fundamental theorem in the theory of functions, that the behaviour of a function in an analytic domain is determined by its singularities outside that domain. In the light of this remark the singularity in $W(R)$ at $R = 0$, mentioned above, is intriguing.

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APPENDIX

MOLECULAR CUSP CONDITIONS IN ELLIPTIC COORDINATES

The starting point in deriving (17) is the non-relativistic Schrödinger equation for the N electrons in the field of the fixed nuclei A and B . The wave function may be regarded as a function of the elliptic coordinates ξ, η, ϕ for each electron, and the internuclear distance R : $\Psi = \Psi(\xi_1, \eta_1, \phi_1; \dots; \xi_N, \eta_N, \phi_N; R)$. Attention is focussed on one electron, say the i th, and the Schrodinger equation written in the form (atomic units)

$$\begin{aligned}
 -\frac{2}{R^2(\xi_i^2 - \eta_i^2)} \left\{ \frac{\partial}{\partial \xi_i} \left[(\xi_i^2 - 1) \frac{\partial \Psi}{\partial \xi_i} \right] + \frac{\partial}{\partial \eta_i} \left[(1 - \eta_i^2) \frac{\partial \Psi}{\partial \eta_i} \right] + \left[\frac{1}{\xi_i^2 - 1} + \frac{1}{1 - \eta_i^2} \right] \frac{\partial^2 \Psi}{\partial \phi_i^2} \right. \\
 \left. + (RZ\xi_i - R\Delta\eta_i) \Psi \right\} + \sum_{j \neq i} \left(-\frac{1}{2} \nabla_j^2 - \frac{Z_a}{r_{aj}} - \frac{Z_b}{r_{bj}} \right) \Psi \\
 + \left(\sum_{i > j} \frac{1}{r_{ij}} - W \right) \Psi = 0, \quad (A.1)
 \end{aligned}$$

where $\Delta = Z_a - Z_b$. The wave function is now expanded in surface harmonics in η_i, ϕ_i :

$$\Psi(\xi_i, \eta_i, \phi_i; \text{etc.}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l (\xi_i^2 - 1)^{|m|/2} P_l^m(\eta_i) e^{im\phi_i} \Psi_{lm}(\xi_i; \text{etc.}); \quad (A.2)$$

the factor involving $(\xi_i^2 - 1)$ is necessary in order that Ψ can be an eigenfunction of (A.1), and has merely been exhibited explicitly

for convenience. By substituting (A.2) into (A.1), the large term in curly brackets becomes

$$\{i\} = \sum_l \sum_m (\zeta_i^2 - 1)^{lm/2} P_l^m(\eta_i) e^{im\phi_i} \left[(\zeta_i^2 - 1) \frac{\partial^2 \Psi_{lm}}{\partial \zeta_i^2} + 2(\zeta_i + 1/m) \frac{\partial \Psi_{lm}}{\partial \zeta_i} + [m^2 - l(l+1)] \Psi_{lm} \right]. \quad (\text{A.3})$$

Equation (A.1) is now integrated over all values of η_i, ϕ_i , to pick out the zero Legendre component. By using equations (12), and rearranging, the result may be written

$$\sum_{k=0}^{\infty} \zeta_i^{-1} \left[Q_{2k}(\zeta_i) \left\{ (\zeta_i^2 - 1) \frac{\partial^2 \Psi_{2k,0}}{\partial \zeta_i^2} + 2\zeta_i \frac{\partial \Psi_{2k,0}}{\partial \zeta_i} + (R^2 - 2k(2k+1)) \Psi_{2k,0} \right\} - Q_{2k+1}(\zeta_i) R \Delta \Psi_{2k+1,0} \right] - \frac{1}{4} R^2 \left(\iint \mathcal{H}' \Psi d\eta_i d\phi_i - W \Psi_{0,0} \right) = 0, \quad (\text{A.4})$$

where \mathcal{H}' is the part of the electronic Hamiltonian left over in equation (A.1) after removal of the one-electron terms for electron i . Consider now the limit $\zeta_i \rightarrow 1$. The term involving $\mathcal{H}' \Psi$ is finite, at least provided that $\zeta_j \neq 1$ for any other electron j , and no two electrons are at the same point in space. However, the term involving the Legendre functions diverges logarithmically, since

$$\lim_{\zeta \rightarrow 1} [Q_l(\zeta)] = Q_0(\zeta) = \frac{1}{2} \log \left(\frac{\zeta+1}{\zeta-1} \right) \rightarrow +\infty. \quad (\text{A.5})$$

Since the Schrodinger equation must be valid for all ξ_i , it follows that

$$\sum_{k=0}^{\infty} \left\{ 2 \frac{\partial \Psi_{2k,0}}{\partial \xi_i} \bigg|_{\xi_i=1} + (R^2 - 2k(2k+1)) \Psi_{2k,0}(\xi_i=1) - R \Delta \Psi_{2k+1,0}(\xi_i=1) \right\} = 0. \quad (A.6)$$

A similar relation may be deduced involving the derivatives of the odd components with respect to ξ_i , but is not required here.

This infinite sum is not attractive by comparison with the simple cusp conditions for the zero (symmetric) $\cos \theta_a$ - and $\cos \theta_b$ -components of the molecular wave function at nuclei A and B, namely¹⁸

$$\left(\frac{\partial \Psi_{0,0}^A}{\partial r_{Ai}} \right)_{i=A} = -Z_A \Psi_{0,0}(i=A), \quad \left(\frac{\partial \Psi_{0,0}^B}{\partial r_{Bi}} \right)_{i=B} = -Z_B \Psi_{0,0}(i=B). \quad (A.7)$$

Nevertheless it is condition (A.6) that is needed and not conditions (A.7).

Consider the form of (A.6) for small R. In the limit as $R \rightarrow 0$ the molecular wave function $\Psi = \Psi^{\text{mol}}$ becomes the united atom wave function Ψ^{UA} , and the l th η_i -component of Ψ^{mol} becomes the l th $\cos \theta_i$ -component of Ψ^{UA} , Ψ_{l0}^{UA} . Since Ψ^{UA} is an analytic function of r_i , it follows that $\Psi_{l0}^{\text{UA}}(r_i; \text{etc})$ is of order r_i^l in r_i . Hence $\Psi_l^{\text{mol}}(\xi_i; \text{etc})$ is of order $(R\xi_i/2)^l$ when R is small. By analyzing (A.6) in this manner it can be seen that

$$2 \left. \frac{\partial \Psi_{00}}{\partial \xi_i} \right|_{\xi_i=1} + R Z \Psi_{00}(\xi_i=1) = O(R^2). \quad (\text{A.8})$$

It is now straightforward to repeat the analysis used by Steiner¹³ in the atomic case, and derive the cusp condition (17) for the electron density component $\rho_0(\xi; R)$.

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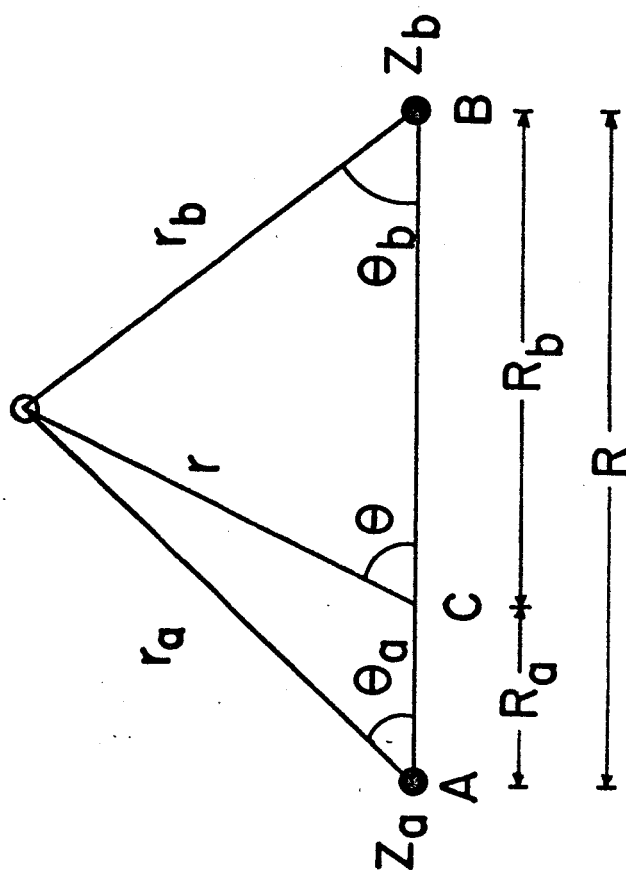


Figure 1.

Diagram defining the coordinates used in describing interacting atoms A and B at distance R apart. C is the centre of nuclear charge.

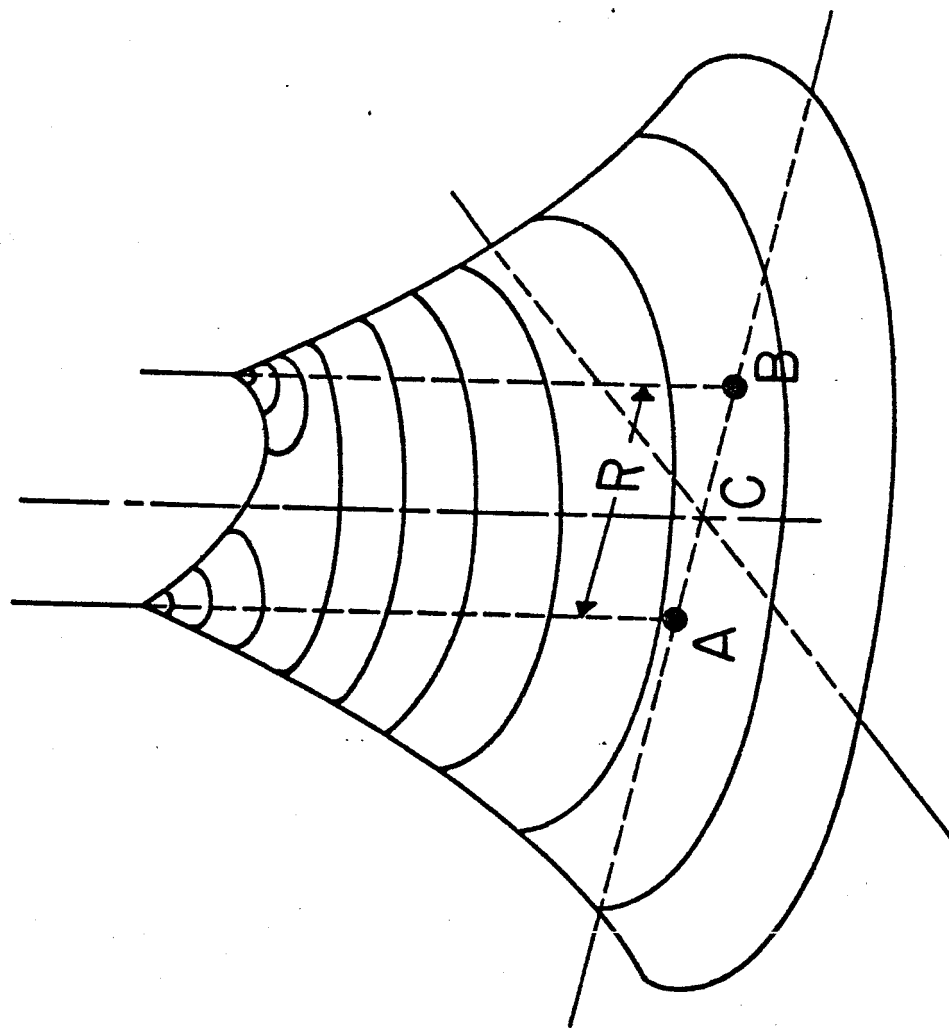


Figure 2.

(a)

Sketch of electron density surface $\rho(\xi, \eta; R)$ over the $\xi\eta$ -plane through the interatomic axis AB , with $Z_a > Z_b$; ordinary value of R

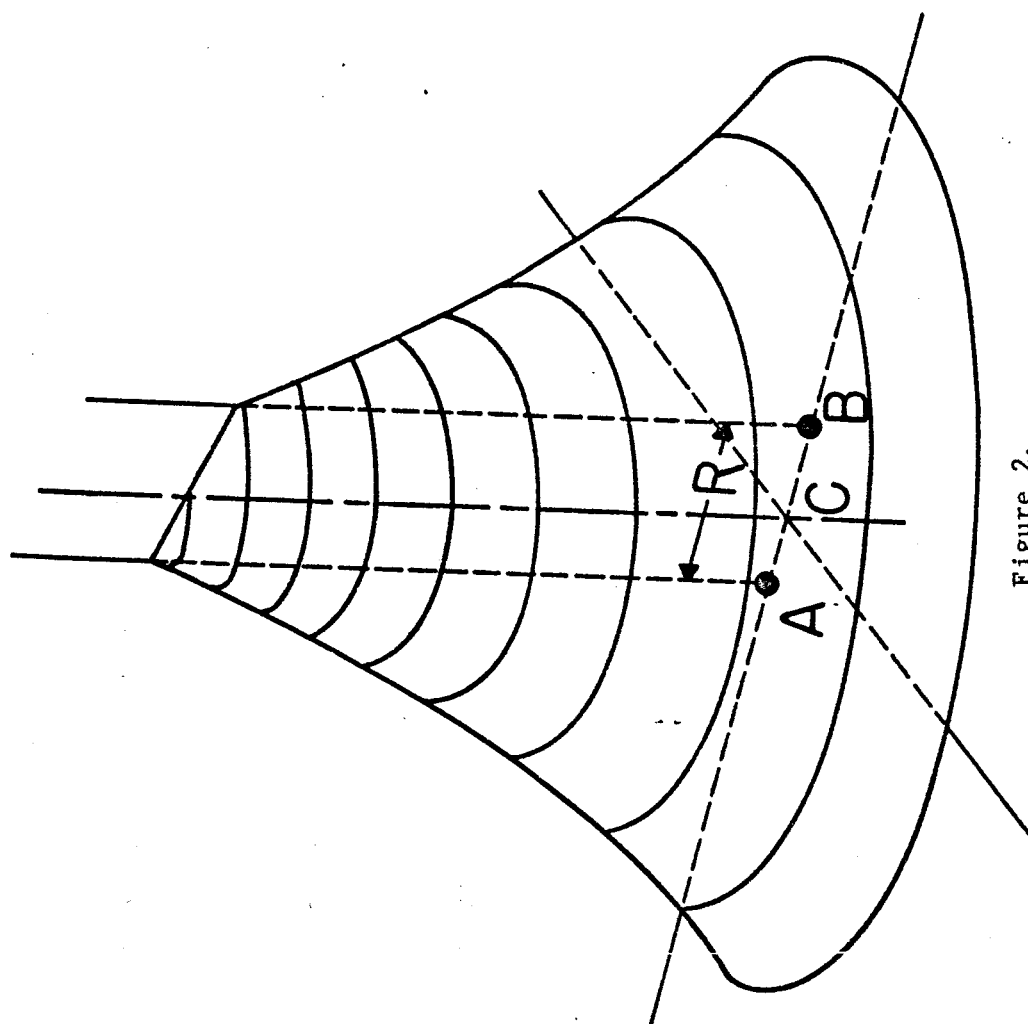


Figure 2.

(b)

Sketch of electron density surface $\rho(\xi, \eta; R)$ over the $\xi\eta$ -plane through the interatomic axis AB, with $Z_a > Z_b$; very small R .

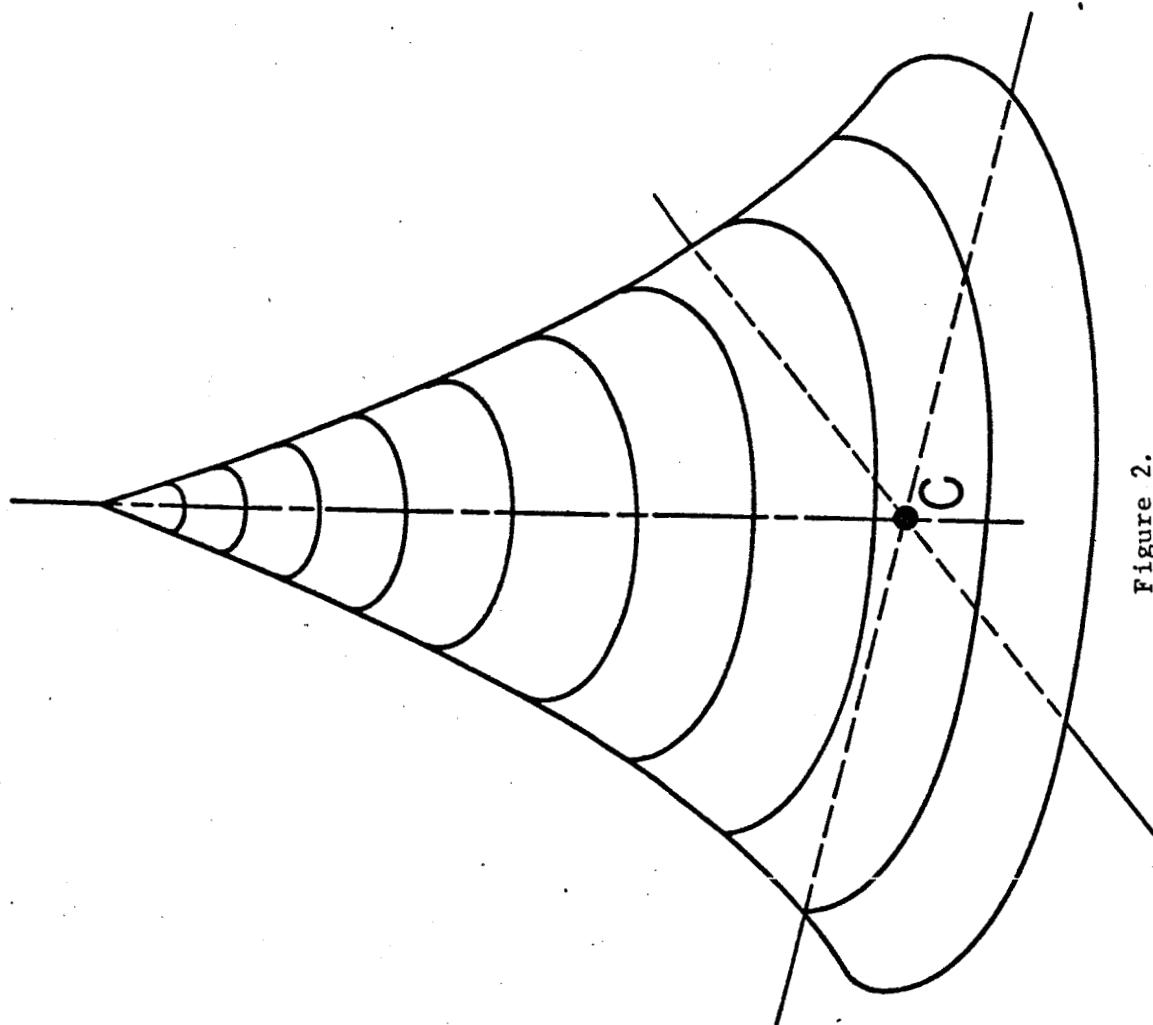


Figure 2.

(c)

Sketch of electron density surface $\rho(\xi, \eta; R)$ over the $\xi\eta$ -plane through the interatomic axis AB, with $Z_a > Z_b$; united atom, $R = 0$.

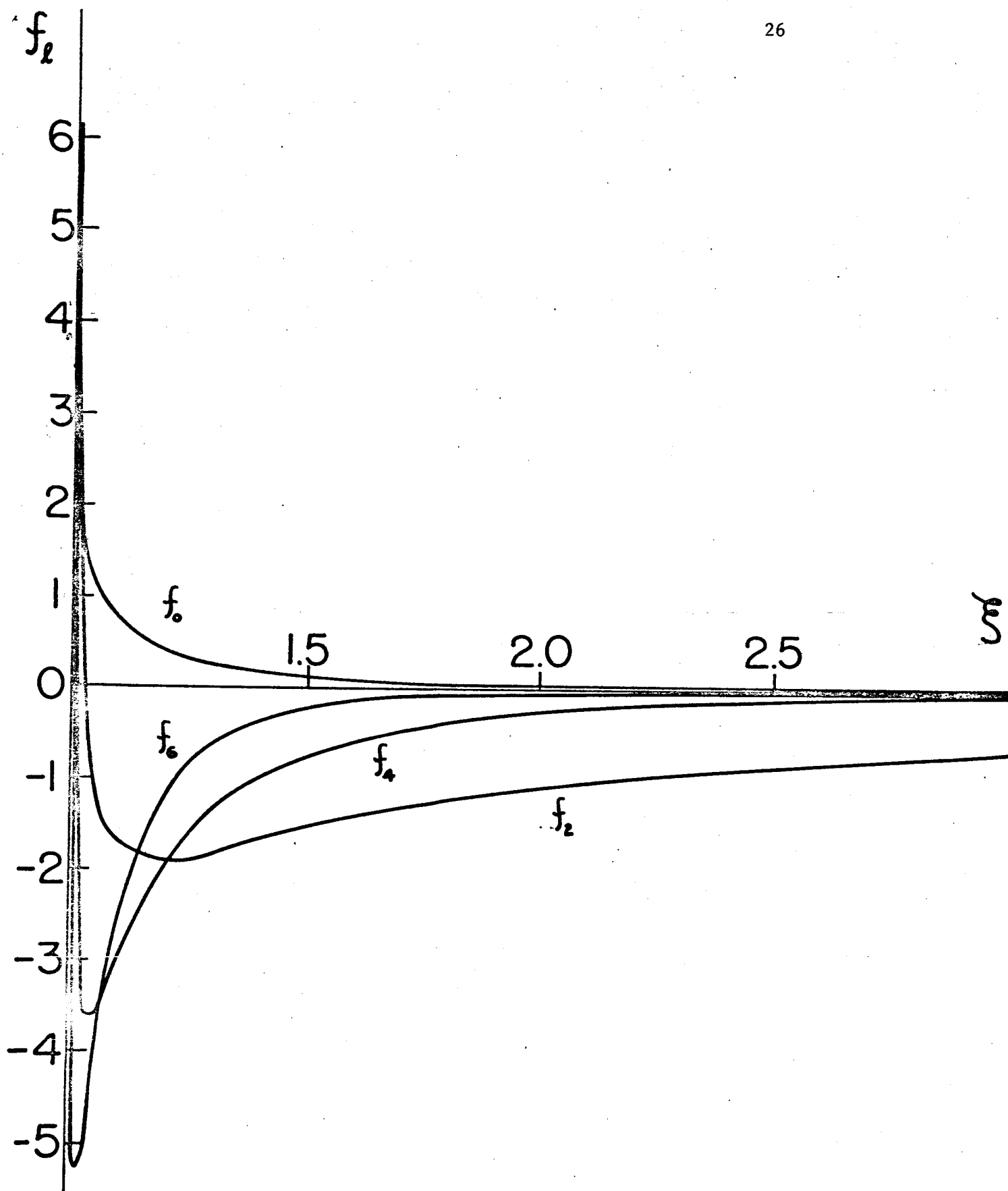


Figure 3.

Graph of first four elliptic force operator components $f_l(\xi)$ ($l=0, 2, 4, 6$) defined by equation (13), plotted against ξ (range $(1, \infty)$).